any other gravimetric procedure which has been employed for the separation of these metals the electrolytic method is superior in every particular. It is readily executed, it requires less time, and the results afforded by it are most satisfactory. Finally, the separation of manganese from zinc, as described above, is of practical value.

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ON A COLORIMETRIC METHOD FOR THE ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.[1]

BY OSWALD SCHREINER.

THE estimation of small amounts of phosphates in waters and aqueous extracts of soils and plants is a matter of daily occurrence in the study of field conditions of the soils, of surface and subsurface waters and growing crops, as carried on in the Bureau of Soils, U. S. Dept. of Agriculture. The method first used by Lepierre,[2] also by Jolles and Neurath,[3] and perfected by Woodman and Cayvan,[4] Veitch,[5] and others, consisted in measuring the color developed by phosphates with ammonium molybdate in nitric acid solution against a known solution of phosphate as standard. As silica gives the same coloration with this reagent, its almost unfailing presence in natural waters is a disturbing factor. In the Woodman and Cayvan method, the silica is removed by evaporating once or twice to dryness with nitric acid and heating for two hours in an oven at 100°. The phosphate is then dissolved and separated from the insoluble silica by filtration, and estimated colorimetrically. The need of a more rapid field method induced Prof. F. H. King, Chief of the Division of Soil Management, to direct the investigation of silica and phosphate solutions, which has led to the method here reported.

In the method given in the following pages, the silica is estimated simultaneously with the phosphates. The method is based on the experimental observation that silica solutions will give different intensities of coloration under different conditions, while phosphates give the same coloration under these different con-

[1] Published by permission of the Secretary of Agriculture.

[2] *Bull. Soc. Chim.*, **15**, 1213.

[3] *Monatsh. Chem.*, **19**, 5.

[4] This Journal, **23**, 96.

[5] *Ibid.*, **25**, 169.

ditions. When, as is usually done in the colorimetric estimation of phosphates, the nitric acid and ammonium molybdate solutions are added simultaneously to the silica solution, a certain intensity of color is developed. If, however, the ammonium molybdate reagent is added to the silica solution, and after a period of time the nitric acid, the intensity of color produced by the same amount of silica is far less than in the first case. Experiments have shown that the solution must stand at least one hour with the ammonium molybdate reagent before adding the nitric acid, in order to get the maximum effect. Some color is developed by the ammonium molybdate alone, but this is greatly influenced by the presence of other salts, temperature, etc., but on adding the nitric acid it always comes up to a definite intensity of color, which is approximately only one-half of the color developed when both reagents are added simultaneously. This different coloration of the silica solutions under these conditions is undoubtedly due to the formation of decidedly different silico-molybdates. Phosphates under these two conditions give exactly the same intensity of color.

<div align="center">REAGENTS.</div>

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid* (sp. gr. 1.07).

(3) *Standard Phosphate Solution.*—0.5045 gram of pure, freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. $= 0.0001$ gram P_2O_5.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting 10 cc. of the above standard phosphate solution to about 80 cc. and then adding 9 cc. of nitric acid (sp. gr. 1.07), and 8 cc. of ammonium molybdate reagent and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5.

COLORIMETER.

The instrument used was similar to the one described and illustrated by Whitson.[1] It consists of a tube of colorless glass, 1 inch by 10 inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution; a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cc. and 100 cc. mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cc. mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

EQUIVALENCE OF THE SILICA COLORATIONS.

To determine the equivalence of the silica colorations, both an alkaline and a neutralized solution of silica were used. The first was prepared by dissolving silica in sufficient solution of sodium hydroxide, made by the action of sodium on water in a platinum dish, to make Na_2SiO_3, and the second by dissolving crystallized Na_2SiO_3 in water and neutralizing with nitric acid. The strength of both solutions was accurately determined gravimetrically and then diluted.

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN BOTH REAGENTS ARE ADDED SIMULTANEOUSLY.

To 50 cc. of the silica solution, 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent were added, and after twenty minutes compared with the standard colorimetric solution in the colorimeter. If the amount of color developed was too great for a safe reading, the solution was diluted and an aliquot part taken and read. The results are given in the following table:

[1] Bulletin 85, Wis. Agr. Expt. Station.

SOLUTION OF $Na_2SiO_3 + 2HNO_3$.

SiO$_2$ present. mg.	P$_2$O$_5$ required to equal color produced by SiO$_2$. mg.	1 mg. of P$_2$O$_5$ equals mg. of SiO$_2$.
0.0826	0.1580	0.523
0.0826	0.1570	0.526
0.1652	0.3170	0.521
0.3303	0.6140	0.538
0.4139	0.7575	0.546
0.6606	1.2600	0.524
0.8258	1.5000	0.551
0.8258	1.5300	0.540

SOLUTION OF $SiO_2 + 2NaOH$.

0.0897	0.1835	0.489
0.3588	0.7220	0.497
0.8970	1.7350	0.517

Average, 0.525

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN THE AMMONIUM MOLYBDATE REAGENT IS ADDED ONE HOUR BEFORE THE NITRIC ACID.

To 50 cc. of the silica solution, 4 cc. of the ammonium molybdate reagent were added, and after standing one hour 5 cc. of the nitric acid reagent. After twenty minutes, readings were made as before. The results appear in the following table:

SOLUTION OF $Na_2SiO_3 + 2HNO_3$.

SiO$_2$ present. mg.	P$_2$O$_5$ required to equal color produced by SiO$_2$. mg.	1 mg. of P$_2$O$_5$ equals mg. of SiO$_2$.
0.1652	0.1490	1.109
0.1652	0.1500	1.101
0.3303	0.3050	1.083
0.3303	0.3075	1.074
0.6606	0.5820	1.135
0.8258	0.7300	1.131

SOLUTION OF $SiO_2 + 2NaOH$.

0.0897	0.0900	0.997
0.3588	0.3500	1.025
0.8970	0.9075	0.988

Average, 1.071

RELATION BETWEEN THE TWO SiO_2 VALUES.

Examining the two silica values for each solution it will become apparent that one is approximately one-half the other. Taking the average value of each type this relation becomes

$$\frac{0.525}{1.071} = 0.49 \text{ or } \frac{1.071}{0.525} = 2.04.$$

The relation of the two silica colorations to each other is, therefore, for all practical purposes, one-half, and this value is used in the following equations for the method.

METHOD FOR THE DETERMINATION OF PHOSPHATES IN THE PRESENCE OF SILICATES.

On the different behavior of silica solutions towards ammonium molybdate under conditions which produce no change in the effect of this reagent on phosphates may be based a method for determining phosphates and silicates when both are present in a solution. There are in solution two unknown quantities; namely, silica (x) and phosphate (y). It has been shown that under a certain condition the silica gives a colorimetric reading which is only one-half as great as under another condition, whereas the phosphates give the same reading under either condition. Hence, when a solution containing both phosphates and silica is subjected to both these conditions, one reading will be obtained under one condition and another reading under the other condition, the differences in the readings being due entirely to the silica. There are, consequently, two equations, and having only two unknown quantities, these can be readily found. These two equations are:

$$(1) \quad x + y = a,$$
$$(2) \quad \tfrac{1}{2}x + y = b,$$

where (x) is the silica reading and (y) the phosphate reading, and (a) the experimental reading obtained under one condition, and (b) the experimental reading obtained under the other condition.

The working of this method is as follows:

Determination of the "a" Reading.—To 50 cc. of the solution add 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent, and after twenty minutes the colorimetric reading is made. This gives the "a" reading in equation (1).

Determination of the "b" Reading.—To a second portion of 50 cc. of the solution add 4 cc. of ammonium molybdate solution and allow to stand one hour. At the end of this time add 5 cc. of nitric acid reagent and after twenty minutes read in the colorimeter. This gives the "b" reading in equation (2).

From these two readings the true phosphate (y) and silica (x) readings are readily calculated. The silica reading is twice the

difference between the "*a*" and "*b*" readings. To get the silica in milligrams of SiO_2, multiply the reading by 0.00525. The phosphate reading is the difference between the "*a*" reading and the silica reading. To get the phosphate in milligrams of P_2O_5 multiply by 0.01.

APPLICATIONS OF THE METHOD.

The method was tested on known solutions of phosphates in the presence of silicates. The results were as follows:

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2.	P_2O_5.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
3.30	2.00	82.6	50.9	63.4	19.2	3.33	1.92
9.91	20.00	410.0	309.0	202.0	208.0	10.60	20.80

A known phosphate solution containing also the salts usually found in soil solutions or natural waters, silicates, sulphates, bicarbonates, chlorides, and nitrates was prepared and estimated.

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2.	P_2O_5.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
3.30	2.00	85.0	52.0	66.0	19.0	3.46	1.90

The method was further tested on some standard salts which had been prepared for field investigations and contained known amounts of phosphates, besides silicates and other salts. These salts were dissolved in water and the solutions estimated. The results were:

	P_2O_5.		p. p. m. of P_2O_5 in solution.		
No.	Present. mg.	Found. mg.	Present.	Found.	p. p. m. of SiO_2.
1	0.535	0.536	10.70	10.72	4.18
2	0.520	0.532	10.40	10.64	4.65
3	0.550	0.522	11.00	10.44	4.26
4	0.468	0.471	9.36	9.42	3.70
5	0.480	0.451	9.60	9.02	4.04
6	0.525	0.506	10.50	10.12	4.26

The phosphates and silica in a well-water were determined. The amount of phosphates in proportion to the silica in this water is quite small, and its determination is, therefore, affected by the unavoidable error of reading. The results obtained with duplicates were as follows:

	Readings for 100 cc.		Readings for		p. p. m.	
No.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
1	374.0	192.5	363.0	11.0	19.1	1.1
2	370.0	193.0	354.0	16.0	18.7	1.6
				Average,	18.9	1.35

To this same well-water a known amount of phosphate was added and again estimated. The calculated p. p. m. of P_2O_5 is the sum of the p. p. m. added (10), and the average result obtained above (1.35).

No.	Readings for 100 cc.		Readings for		p. p. m. found.		p. p. m. calculated.	
	"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
1....	454	281	346	108	18.2	10.8	18.9	11.35
2....	455	285	340	115	17.9	11.5	18.9	11.35

A soil solution was prepared by washing 100 grams of soil with 500 cc. of water and filtering through a Chamberland filter. The resulting colorless solution was analyzed.

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
203	142	122	81	6.4	8.1

To this same soil solution 5 p. p. m. of P_2O_5 was added and again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	P_2O_5.
254	192	124	130	6.5	13.0	13.1

A plant solution was prepared by washing 20 grams of corn plant with 500 cc. of water. The decolorization of the solution was effected by means of charcoal. The result found was as follows:

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
450	389	122	328	6.4	32.8

To this same plant solution a known amount of phosphates was added (10 p. p. m.) and the solution again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
547	484	126	421	6.6	42.1	6.4	42.8

It is highly essential for these colorimetric tests that all plant and soil solutions be absolutely colorless.

BUREAU OF SOILS, U. S. DEPARTMENT OF
    AGRICULTURE, WASHINGTON, D. C.